

Synthesis of a New NP Multi-Site Phase-Transfer Catalyst and Its Application to Dichlorocarbene Addition Reactions

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ABSTRACT

This work describes the preparation of a new NP multi-site phase-transfer catalyst was obtained from the reaction of triphenylphosphine, 1,4-dibromobutane and tributylamine. Using this new multi-site phase-transfer catalyst the dichlorocarbene addition reactions were carried out with different alkenes in an alkaline solution/chloroform two phase medium.

Keywords: Multi-site phase-transfer catalyst; dichlorocarbene addition reaction; liquid-liquid bi-phase reaction; aqueous-organic reaction; heterogeneous reaction.

1. INTRODUCTION

Phase-transfer catalysis (PTC) was originally developed in mid-1960's to enhance chemical reactions catalyzed by quaternary ammonium salts in which the reactants are in two separate phases¹. By now, the phase-transfer catalyst is now considered to be one of the most effective tools for organic synthesis from two or more immiscible solutions²⁻⁴. The methodology of phase-transfer catalysis involves an organic-soluble reactant and an aqueous-soluble anionic reactant and the water-soluble anion are then brought together by a catalyst, which transports the anion into the organic

phase where reaction takes place with the organic reactant. Quaternary ammonium and phosphonium salts with their unique capability to dissolve in both aqueous and organic liquids are the catalysts of choice for most phase-transfer applications⁵. The benefits of PTC lie in the elimination of organic solvents and dangerous or expensive bases, together with simplicity of the procedure, and its high yields and the purity of the products. This is particularly attractive due to the increasing number of environmental laws since PTC processes always produce much less industrial waste and consume less energy than traditional processes.

Idoux *et al.*⁶ first reported the soluble and insoluble phosphonium ion containing multi-site PTCs. Recently, several soluble multi-site ammonium catalysts have been synthesized⁷⁻¹⁰. Catalysts such as these have the advantage over single-site catalysts in reactions involving divalent anions that they generally need less of the salt to obtain a catalytic effect. In general, multi-site phase-transfer catalysts have a greater phase-transfer catalytic activity than the single-site one^{7,10,11}. To our knowledge, literature survey reveals that the multi-site phase-transfer catalysts containing either phosphonium cation active sites or ammonium cation active sites only. There is no report for a multi-site phase-transfer catalyst containing both ammonium and phosphonium active site ions. So we have first time synthesized a new multi-site phase-transfer catalyst containing ammonium and phosphonium active sites within the same catalyst. So hereafter it is called NP multi-site phase-transfer catalyst (NPMSPTC). The catalytic activity of the newly synthesized NP multi-site PTCs was tested towards the dichlorocarbene addition reactions with different olefins under bi-phase condition.

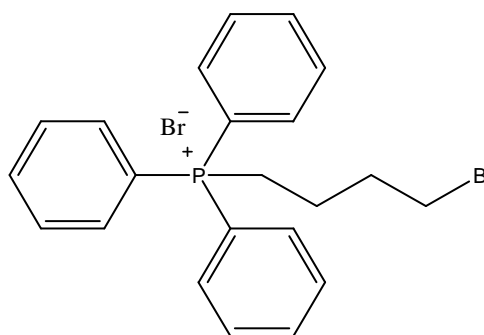
2. EXPERIMENTAL

2.1 Materials

All reagents, triphenyl phosphine, 1,4-dibromobutane, tributylamine, diethyl ether, sodium hydroxide, chloroform, styrene, p-methyl styrene, 1-pentene, 1-hexene, 1-heptene, 1-octene, cyclopentene, cyclohexene, cyclooctene, allyl phenyl ether etc., were guaranteed grade (GR) chemicals, and were used as received without further purification.

2.2 Synthesis of 1-triphenylphosphonium-4-bromobutyl bromide (C₂₂H₂₃PBr₂)

A mixture of 13.12 g (0.05 mol) of triphenylphosphine, 25.92 g (0.12 mol) of 1,4-dibromobutane, and 150 ml of acetonitrile was placed in a 250 ml three-necked round bottomed Pyrex flask. The mixture was stirred continuously using a mechanical mixer equipped with a poly(tetrafluoroethylene) half-moon blade agitating at 600 rpm. The reaction was carried out at 70°C for 48 h under nitrogen atmosphere. Then, the solvent was removed by a vacuum evaporator. A white solid of 1-triphenylphosphonium-4-bromobutyl bromide (structure 1) was obtained which is stored in CaCl₂ desiccator. The product was identified with an elemental analyzer and ¹H NMR for functional groups. The elemental analysis of carbon, and hydrogen was performed with an Elementar Vario EL elemental analyzer. The results obtained from elemental analysis were as follows: C_{found}, 54.82 %; C_{calcd}, 55.21 %; H_{found}, 4.92 %; H_{calcd}, 4.85 % . ¹H NMR (300 MHz, CDCl₃): δ 7.72-7.88 (Ar H, m, 15 H), δ 3.93 (P⁺ CH₂, t, 2H), δ 3.58 (P⁺ CH₂ CH₂, m, 2H), δ 2.18 (P⁺ CH₂ CH₂CH₂, m, 2H), δ 2.52 (P⁺ CH₂ CH₂CH₂CH₂Br, t, 2H).

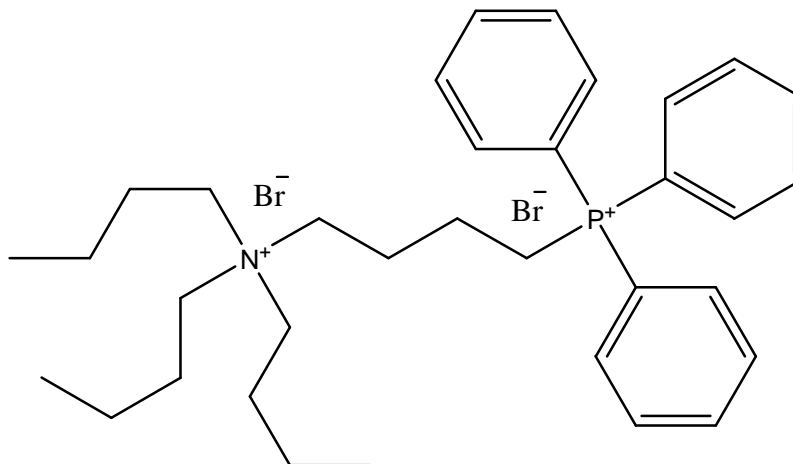


Structure 1: 1-Triphenylphosphonium-4-bromobutyl bromide

2.3 Synthesis of Triphenyl (4-(tributylammonio) butyl) phosphonium dibromide ($C_{34}H_{50}NPBr_2$)

The title compound i.e., triphenyl(4-(tributylammonio)butyl)phosphonium dibromide, NPMSPTC, was prepared by the treatment of 24.0 g (0.05 mol) of 1-triphenyl-phosphonium-4-bromobutyl bromide with 18.56 g (0.1 mol) of tributylamine, and 150 ml of acetonitrile was placed in a 250 ml three-necked round-bottomed Pyrex flask. The reaction mixture was refluxed at 80°C in an oil bath for 48 h under nitrogen atmosphere. To the cold reaction mixture, diethyl ether (3 x 50 ml) was added and the precipitate was collected. Then the pure white solid ammonium phosphonium – multisite phase-transfer catalyst, NPMSPTC (structure 2) was

repeatedly washed (three times) with diethyl ether and then stored in a $CaCl_2$ desiccator. The NPMSPTC were identified with 1H NMR and an elemental analyzer. C_{found} , 60.86 % ; C_{cald} , 61.49 % ; H_{found} , 7.66 % ; H_{cald} , 7.60 % ; N_{found} , 2.14 % ; N_{cald} , 2.11 % ; 1H NMR (300 MHz, $CDCl_3$): δ 7.72-7.88 (Ar H, m, 15 H); δ 3.92 (P^+CH_2 , t, 2H); δ 3.56 ($P^+CH_2CH_2$, m, 2H); δ 2.16 ($P^+CH_2CH_2CH_2$, m, 2H); δ 3.88 (N^+CH_2 , t, 8H); δ 3.62 ($N^+CH_2CH_2$, m, 6H); δ 2.34 ($N^+CH_2CH_2CH_2$, m, 6H); δ 1.08 ($N^+CH_2CH_2CH_3$, t, 9H). Elemental analysis of carbon, hydrogen, and nitrogen was performed with an Elementar Vario EL elemental analyzer. 1H NMR (300 MHz) was recorded on a BRUCKER-AM-300 NMR spectrometer with TMS as an internal standard. FT-IR; 1178 cm^{-1} (C-N $^+$).



Structure 2: Triphenyl(4-(tributylammonio)butyl)phosphonium dibromide

3. RESULTS AND DISCUSSION

In order to investigate the efficiency of the new quaternary ammonium phosphonium multi-site phase-transfer

catalyst (NPMSPTC) under study, dichlorocarbene ($:CCl_2$) addition to different olefins have been chosen. The results shown in Table 1. In the absence of the phase-transfer catalyst less than 1 % conversion

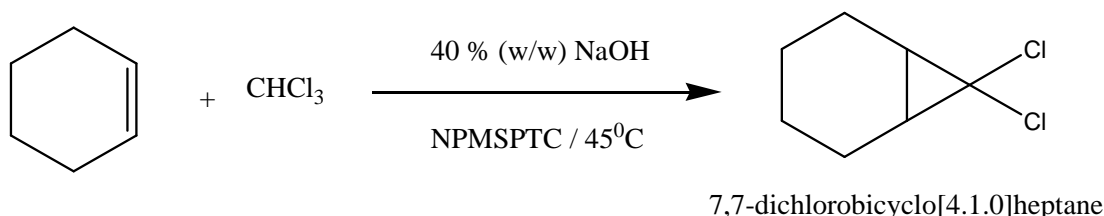
is detected (even after 3 h of reaction) by gas chromatography. Excellent yields of products were obtained in 2 h on using 2 mol% (based on the substrate amount) of the new catalyst. Thus revealing the remarkable efficiency of NPMSPTC as potential phase-transfer reagent.

3.1 General procedure for the dichlorocarbene (:CCl₂) addition to olefins using the new phase-transfer catalyst, NPMSPTC.

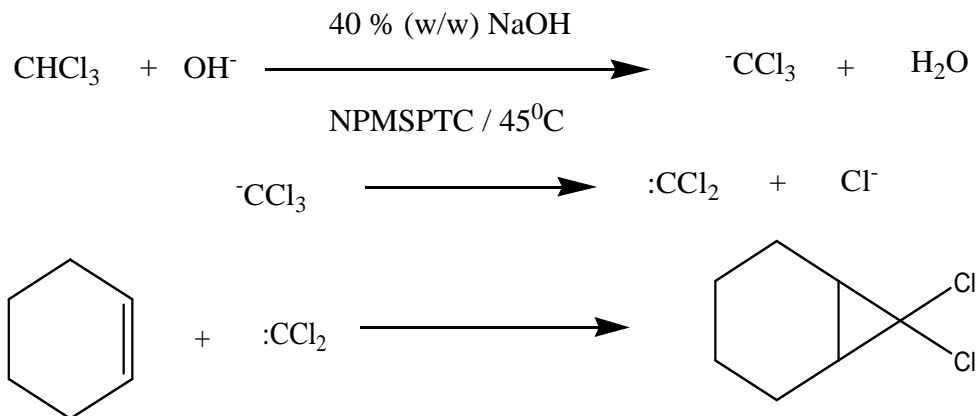
The reactor was a 250 ml three-necked round bottomed Pyrex flask was charged with 30 ml (40 % w/w) sodium hydroxide, 2 mol% of the phase-transfer catalyst (based on the substrate amount), chloroform 25 ml and biphenyl (0.5 g,

internal standard). The ingredients were conditioned for 10 min in the thermostat maintained at 45°C. Olefin (0.5 ml) was added to the reaction mixture and stirred for 2 h at 600 rpm. The sample (0.5 ml) was withdrawn periodically from the reactor and put into the glass vials containing 2 ml of chloroform. The samples were then analyzed by gas chromatography (GC–shimadzu 17 A model). The analyzing conditions were as follows: 30 m x 0.525 mm i.d. capillary column containing 100 % poly(dimethyl siloxane); injection temperature, 250°C; flame ionization detector (300°C). Yields were determined from standard curve and using biphenyl as internal standard. The detailed reaction mechanism for cyclohexene (olefine) is given in scheme 1.

Reaction:

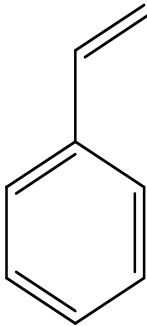
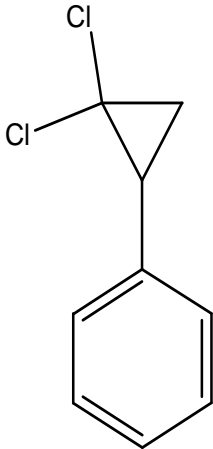
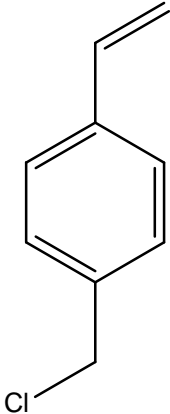
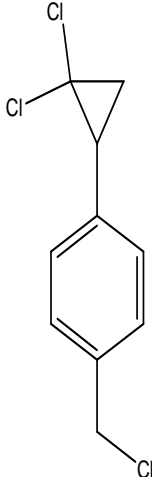


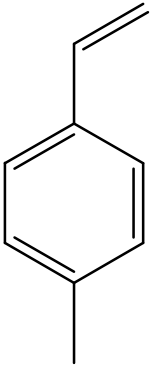
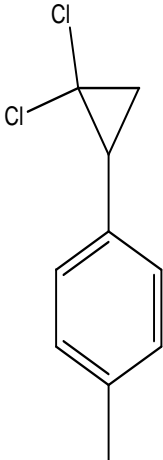
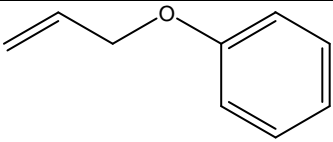
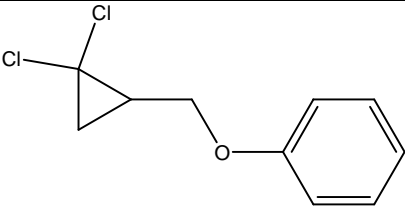
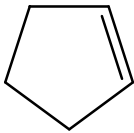
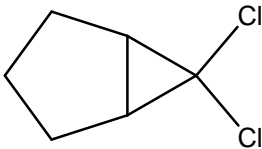
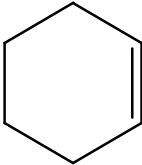
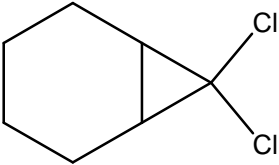
Mechanism:

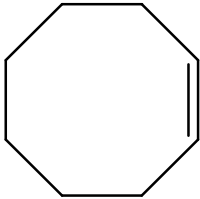
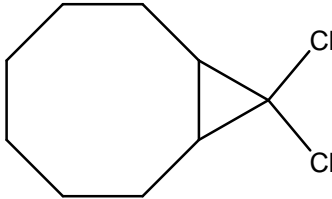
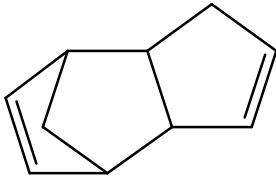
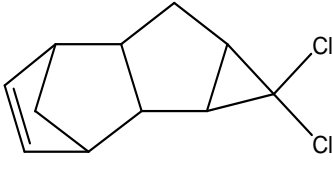
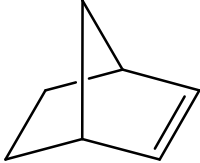
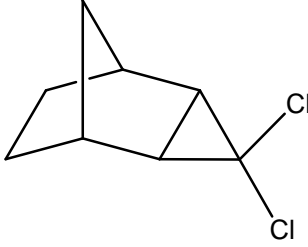
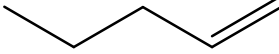
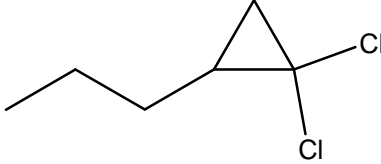
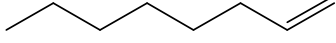
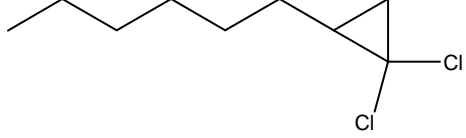


Scheme 1

Table 1: Dichlocarbene addition to olefins using NPMPTC

S. No.	Substrate	Product	% Conversion
1	 Styrene	 1-phenyl-2,2-dichloro cyclopropane	92
2	 p-chloromethylstyrene	 1-(4-chloromethyl phenyl)-2,2-dichlorocyclopropane	84

3	 <p>p-methylstyrene</p>	 <p>1-(4-methyl phenyl)-2,2-dichlorocyclopropane</p>	96
4	 <p>Allyl phenyl ether</p>	 <p>1-((2,2-dichlorocyclopropyl)methoxy)benzene</p>	84
5	 <p>Cyclopentene</p>	 <p>6,6-dichloro-bicyclo[3.1.0] hexane</p>	88
6	 <p>cyclohexene</p>	 <p>7,7-dichloro bicyclo[4.1.0] heptane</p>	90

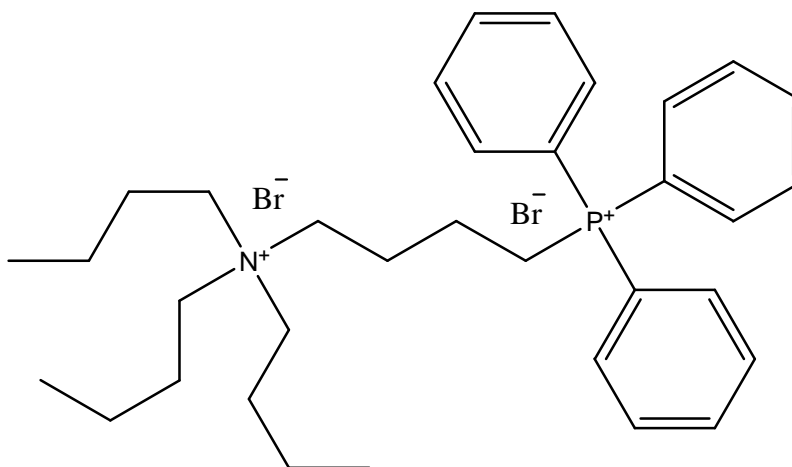
7	 cis cyclooctene	 9,9-dichloro-bicyclo[6.1.0] nonane	82
8	 Dicyclopentadiene	 Dicyclopentenyl-1,1-dichlorocyclopropane	95
9	 bicyclo[2.2.1]hept-2-ene	 3,3-dichlorocyclopropyl norbornane	72
10	 1-pentene	 1,1-dichloro-2-propylcyclopropane	90
11	 1-octene	 1,1-dichloro-2-hexylcyclopropane	95

a: % conversion by gas chromatography.

Graphical Abstract

Synthesis of a New NP Multi-Site Phase-Transfer Catalyst and Its Application to Dichlorocarbene Addition Reactions

A detailed account of the synthesis of a new soluble hetero multi-site quaternary phase-transfer catalyst (NPMSPTC) was synthesized and characterized. The catalytic activity of this catalyst was tested for dichlorocarbene addition to various olefins under bi-phase condition. It shows a good catalytic activity towards dichlorocarbene addition reaction to various olefins.



Triphenyl(4-(tributylammonio)butyl)phosphonium dibromide (NPMSPTC)

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REFERENCES

1. Starks C. M., *J. Am. Chem. Soc.* 93 195 (1971).
2. Starks C. M., Liotta C. L. and Halpern, M., *Applications and Industrial perspectives*, Chapman & Hall Publications, New York, USA (1994).
3. Dehmlow E. V. and Dehmlow S. S., *Phase-transfer catalysis, third ed.*, VCH, New York, USA (1993).

4. Sasson Y. and Neumann R. (Eds.) *Handbook of Phase Transfer Catalysis*, Blackie Academic and Professional, London, UK (1997),
5. Jones R. A. (Ed.) *Quaternary Ammonium salts: Their use in Phase-Transfer Catalyzed Reactions*, Academic Press, U K (2001).
6. Idoux J. P., Wysocki W., Young S., Turcot J., Ohlman C. and Leonard R., *Synth. Commun.* 13 139 (1983).
7. Wang M. L. and Hsieh Y. M., *J. Mol. Cat. A: Chemical* 210 59 (2004).
8. Lissel M., Feldman D., Nir M. and Rabinovitz M., *Tetrahedron Lett.* 30 1683 (1989).
9. Alvarez-Builla J., Vaquero J. J., Navio J. L. G., Cabello J. F., Sunkel C., Gasa-Juana M. F. D., Dorrego F. and Santos. L., *Tetrahedron* 46 967 (1990).
10. Wang M. L. and Lee Z. F., *Ind. Eng. Chem. Res.* 45 4918 (2006).
11. Jayachandran J. P., Balakrishnan T. and Wang M. L., *J. Mol. Cat. A: Chemical* 152 91 (2000).